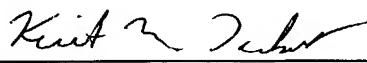


FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER KPTS/6648
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 10/030438
INTERNATIONAL APPLICATION NO. PCT/EP00/06354	INTERNATIONAL FILING DATE 4 JULY 2000 (04.07.2000)	PRIORITY DATE CLAIMED 5 JULY 1999 (05.07.1999)		
TITLE OF INVENTION SYNTHETIC BOTTLE STOPPER				
APPLICANT(S) FOR DO/EO/US COIGNOUL, ET AL.				
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:				
<ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). <input checked="" type="checkbox"/> has been communicated by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> <input type="checkbox"/> is attached hereto. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). <input type="checkbox"/> have been communicated by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input checked="" type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). 				
Items 13 to 20 below concern document(s) or information included: <ol style="list-style-type: none"> <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> Certificate of Mailing by Express Mail <input checked="" type="checkbox"/> Other items or information: 				

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 10/030438	INTERNATIONAL APPLICATION NO. PCT/EP00/06354	ATTORNEY'S DOCKET NUMBER KPTS/6648
24. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :		CALCULATIONS PTO USE ONLY
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00 <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$890.00
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30 \$0.00
CLAIMS	NUMBER FILED	NUMBER EXTRA
Total claims	21 - 20 =	1
Independent claims	2 - 3 =	0
Multiple Dependent Claims (check if applicable).		<input type="checkbox"/> \$0.00
TOTAL OF ABOVE CALCULATIONS =		\$908.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.		\$0.00
SUBTOTAL =		\$908.00
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30 + \$0.00
TOTAL NATIONAL FEE =		\$908.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).		<input type="checkbox"/> \$0.00
TOTAL FEES ENCLOSED =		\$908.00
		Amount to be: refunded \$
		charged \$
a. <input type="checkbox"/> A check in the amount of _____ to cover the above fees is enclosed.		
b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>501951/TS6648</u> in the amount of <u>\$908.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed.		
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>501951/TS6648</u> A duplicate copy of this sheet is enclosed.		
d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.		
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.		
SEND ALL CORRESPONDENCE TO:		
Keith M. Tackett Moser, Patterson & Sheridan, LLP 3040 Post Oak Blvd. Suite 1500 Houston, TX 77056 United States of America		
 SIGNATURE <hr/> Keith M. Tackett <hr/> NAME <hr/> 32,008 <hr/> REGISTRATION NUMBER <hr/> 28 December 2001 <hr/> DATE		

10/030438

PATENT
Atty. Dkt KPTS/6648

JC13 Rec'd PCT/PTO 04 JAN 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Coignoul, et al.

§
§ Group Art Unit: Unknown

Serial No.: To Be Assigned

§
§ Examiner: Unknown

Filed: Herewith

§
§
§

For: Synthetic Bottle Stopper

BOX NEW APPLICATION
Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

CERTIFICATE OF MAILING
37 C.F.R. 1.10

I hereby certify that this correspondence is being deposited on
January 4, 2002, with the United States Postal Service as
Express Mail No. EV044735487US, in an envelope addressed
to: BOX NEW APPLICATION, Assistant Commissioner for
Patents, Washington, D.C. 20231.

1/4/02

Kurt R. Zabel

Date

Signature

PRELIMINARY AMENDMENT

Prior to examination, please amend the above-identified application as follows:

IN THE CLAIMS:

Please cancel claims 1 – 10.

Please add the following claims to the application:

11. (New) A synthetic bottle stopper made from a plasticizer-free, foamed thermoplastic elastomer composition comprising:
 - one or more thermoplastic elastomeric block copolymers;
 - one or more branched polyolefins having a melt flow index of from 0.1 to 200 dg/min (at 2.16 kg/190°C, determined in accordance with ASTM D 1238); and
 - a blowing agent.

12. (New) The synthetic bottle stopper of claim 11, wherein said thermoplastic elastomeric block copolymer is a styrenic elastomeric block copolymer.

13. (New) The synthetic bottle stopper of claim 12, wherein said styrenic elastomeric block copolymer contains one or more glassy polymer blocks made of polymerized styrene monomer in an amount of at least 80 mol% on the total monomer content of the glassy block and one or more elastomeric polymer blocks made of polymerized conjugated diene in an amount of at least 80 mol% on the total monomer content of the elastomeric block.

14. (New) The synthetic bottle stopper of claim 13, wherein the conjugated diene is selected from butadiene and isoprene.

15. (New) The synthetic bottle stopper of claim 14, wherein each styrenic elastomeric block copolymer has an overall styrene content of 10 to 50% by weight.

16. (New) The synthetic bottle stopper of claim 15, wherein said styrenic elastomeric block copolymer has a total apparent molecular weight of from 30,000 to 400,000 g/mol.

17. (New) The synthetic bottle stopper of claim 16, wherein said styrenic elastomeric block copolymer is a selectively hydrogenated block copolymer wherein the vinyl content of the conjugated diene block is at least 35 mol% based on the total diene content.

18. (New) The synthetic bottle stopper of claim 17, wherein said styrenic elastomeric block copolymer comprises a triblock copolymer or a mixture of a diblock copolymer and a triblock copolymer.

19. (New) The synthetic bottle stopper of claim 18, wherein said styrenic elastomeric block copolymer comprises a mixture of an S-EB-S triblock copolymer having a total molecular weight of about 50,000 to about 100,000 and an S-EP diblock copolymer having a total molecular weight of about 120,000 to about 200,000.

20. (New) The synthetic bottle stopper of claim 11, wherein said branched polyolefin is selected from the group consisting of a polymer of 1-butene and a high melt strength polymer of propene.
21. (New) The synthetic bottle stopper of claim 20, wherein said branched polyolefin is poly-1-butene having a melt index of about 0.4 dg/min.
22. (New) The synthetic bottle stopper of claim 20, wherein said branched polyolefin is present in an amount of 10 to 100 parts by weight per 100 parts by weight of said thermoplastic elastomeric block copolymers.
23. (New) The synthetic bottle stopper of claim 22, wherein said branched polyolefin is present in an amount of 30 to 80 parts by weight per 100 parts by weight of said thermoplastic elastomeric block copolymers.
24. (New) The synthetic bottle stopper of claim 11, wherein said blowing agent is present in an amount from 1 to 10 %wt, based on the weight of the foamed thermoplastic elastomer composition.
25. (New) The synthetic bottle stopper of claim 24, wherein said blowing agent is selected from the group consisting of azodicarbonamide, sodium bicarbonate, and mixtures thereof.
26. (New) A synthetic bottle stopper made from a plasticizer-free, foamed thermoplastic elastomer composition comprising:
 - 100 parts by weight of a mixture of a selectively hydrogenated styrene/conjugated diene multi block copolymer and a selectively hydrogenated styrene/conjugated diene diblock copolymer;
 - 10 to 100 parts by weight of a branched polyolefin selected from the group consisting of a polymer of 1-butene and a high melt strength polymer of propene, said polyolefin having a melt flow index of from 0.1 to 200 dg/min (at 2.16 kg/190 °C, determined in accordance with ASTM D 1238);

and a blowing agent in an amount of from 1 to 10 percent weight, based on the total weight of the foamed thermoplastic elastomer composition.

27. (New) The synthetic bottle stopper of claim 26, wherein said branched polyolefin is poly-1-butene having a melt index of about 0.4 dg/min.

28. (New) The synthetic bottle stopper of claim 26, wherein said blowing agent is selected from the group consisting of azodicarbonamide, sodium bicarbonate, and mixtures thereof.

29. (New) The synthetic bottle stopper of claim 26, wherein said multi block copolymer is an S-EB-S triblock copolymer and said diblock copolymer is an S-EP diblock copolymer, and wherein the amount of the triblock copolymer is about about 70 to about 90 parts by weight and the amount of the diblock copolymer is about 30 to about 10 parts by weight.

30. (New) The synthetic bottle stopper of claim 29, wherein said S-EB-S triblock copolymer has a total molecular weight of about 50,000 to about 100,000 and said S-EP diblock copolymer has a total molecular weight of about 120,000 to about 200,000.

31. (New) The synthetic bottle stopper of claim 30 having a density less than 0.7 kg/m³.

REMARKS

The above amendments have been made to remove the multiple dependencies in the claims. Early and favorable action in connection with this application is respectfully requested.

Respectfully submitted,


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WO 01/02263

PCT/EP00/06354

SYNTHETIC BOTTLE STOPPER

Field of the Invention

The present invention relates to a synthetic bottle stopper. More in particular, the present invention relates to a bottle stopper made from a foamed thermoplastic elastomer comprising one or more thermoplastic block copolymers and a blowing agent.

5 Background of the invention

Cork is a natural occurring material regularly used for the production of stoppers for casks, vials and 10 bottles (also referred to as "bung" or "moulded closure for a liquid container", etc.). Cork has a good grip on glass, and requires an appropriate force of about 250-430 N to pull off the cork from a bottle. Stoppers made of cork can be used for closing a half-used bottle 15 for a second time. Besides, swell of cork stoppers when in contact with wine improves their grip. Also, cork is a light material (density of about 0.22 kg/m³), which is important to control the cost when transporting the cork and/or the bottles wherein the cork stoppers are used. 20 Cork is hence a popular material in the production of stoppers.

However, stoppers made of cork may become infected by fungi and bacteria, and they may impart undesired flavour and colour to the contents of the vials and bottles 25 wherein they are used. Moreover, good quality cork is becoming rare and hence expensive. Accordingly, synthetic bottle stoppers have been developed.

Obviously, these synthetic bottle stoppers need to perform similar to cork as regards the elasticity of the 30 material, long term creep, good control during insertion and manufacture, and possibility of reinsertion. Most

importantly, they need to be light, i.e., have a density of less than about 0.7 kg/m³, preferably of about 0.5 kg/m³.

Synthetic stoppers for vials and bottles are known.

5 International application 99/01354 (Supreme Corq) discloses a synthetic cork for removable insertion into an opening of a bottle comprising a hard plastic top and a shaft made of a thermoplastic elastomer (TPE) combined with a blowing agent, wherein the TPE consists of one or
10 more styrenic block copolymers. Suitable styrenic block copolymers are selected from the group corresponding to the general formulae A-B or A-B-A, wherein "A" represents a polystyrene block and "B" represents a polybutadiene block, a polyisoprene block, a hydrogenated polybutadiene block or a hydrogenated polyisoprene block. Suitable
15 blowing agents comprise azodicarbonamide or a masterbatch thereof sold under the tradename "SPECTRATECH FM1150H", ozodecarbonoxide and sodium bicarbonate. The mixture used for forming the shaft may also incorporate a minor amount
20 of low density polypropylene.

International application 94/25513 is an earlier application by Supreme Corq, disclosing a synthetic cork (referred to as "molded closure for a liquid container") comprising the TPE and blowing agent mentioned above.

25 US patent No. 3,984,022 (assigned to Le Bouchage Mécanique) discloses a bottle stopper of biconical configuration, which is made from a foamed plastic with a dense outer layer enclosing a closed cellular or honeycomb structure around the centre. The stopper is
30 produced by injection of a plastic material, which may be a polyolefin such as polyethylene or EVA (ethylene-vinyl acetate), with a pore-forming additive into a mould.

35 US patent No. 4,499,141 (assigned to the Coca Cola Company) discloses a plastic closure for sealing liquid product containers wherein a synthetic cork article is

prepared from a thermoplastic resin and a blowing agent, e.g., azodicarbonamide, and whereby the plastic article is injection moulded.

US patent No. 4,188,457 (assigned to Metal Box Limited.) discloses a "bung" for closing a wine bottle in the manner of a cork, which is formed in a conventional injection-moulding machine from ethylene-vinyl acetate copolymer (EVA) with the addition of sodium metabisulphite and sodium bicarbonate.

These synthetic bottle stoppers, however, are either too dense and/or too hard. As a result, these bottle stoppers will be difficult to insert (problem of leakage), and to remove (in one piece) with an ordinary corkscrew. Moreover, it may be difficult to insert a corkscrew if the stopper is too hard. Besides, these synthetic stoppers (or at least those of Supreme Corp) require the presence of a plasticiser in the form of an oil. If no or too little oil is used, then the thermoplastic elastomer composition will be too viscous and the cells therein will not be able to expand. The end-result is a dense "foam". If too much oil is used, then the viscosity will be too low and cells collapse, with the same end-result. Such bottle stoppers therefore require a precise operating window (about 30-40 parts per hundred parts of elastomer). Unfortunately, oil is a potential contaminant of the contents of the bottle. There is therefore a demand for a new foamed thermoplastic elastomer composition that provides synthetic bottle stoppers of suitable density, and that requires no or only a little oil as plasticiser.

Summary of the invention

The present invention provides a synthetic bottle stopper made from a foamed thermoplastic elastomer composition comprising

- a) one or more thermoplastic block copolymers
- c) a blowing agent, and optionally
- d) one or more plasticisers,

characterised in that the composition further comprises

5

- b) one or more branched polyolefins having a melt flow index ('MFI') of from 0.05 to 400 (at 2.16 kg/190 °C, determined in accordance with ASTM D 1238).

Detailed description of the invention

The synthesis of foamed TPE compositions is known. In
10 addition to the references cited herein before, such compositions are described in Japanese patent application No. 58173146 (Yokohama Rubber KK, Derwent abstract No. 83-822911/47). This reference describes a composition comprising a thermoplastic block copolymer and a
15 thermoplastic resin and/or plasticizer or softener. The composition forms a non-adhesive foaming material and can be used as a packing or gasket material.

In US patent No. 4,764,535 (assigned to Q'SO Inc.) a composition is described comprising a mixture of two thermoplastic elastomers, a nucleating agent and an unstable resin. The compositions may be employed in formulating coatings, laminates, hot melt adhesives and caulking compounds.

Hot melt compositions from which foamed products can
25 be obtained are disclosed in US patent No. 4,529,740 (assigned to W.R. Grace&Co.). The compositions include a thermoplastic elastomer, a small amount of a salt of a sulfonated styrene polymer, and a blowing agent. The composition may be used to produce foamed products suited
30 for example as sealants in closures for containers.

Plastic foam products are also disclosed in US patent No. 5,585,411 and International application No. 94/28066 (both to Shell). In the former, a plastic foam is disclosed that is made from a blend comprising poly-1-butene, a styrenic block or star copolymer, and/or an

olefinic rubber, and optionally a non-elastomeric polyolefin. These foams are particularly useful in very high temperature applications such as pipe wrap in refrigerators. In the latter a novel elastomeric poly-1-butene is described, as well as blends thereof with compatible materials, which are particularly suitable in textile and fibre applications, and blends thereof with incompatible materials, which are particularly useful in easy-open packaging applications, in foam applications and in PVC replacement.

The use of a composition as described in claim 1 for the purpose of preparing a superior synthetic bottle stopper is neither disclosed nor hinted at in any of these references. The components of the composition are described in more detail herein after.

Component a)

The expression "thermoplastic block copolymer" refers to a polymer having two or more distinguishable polymer blocks, of which at least one is glassy or crystalline at service temperature but fluid at higher temperatures, and at least one of which is elastomeric (rubbery) at service temperature. A comprehensive review on such polymers is provided by Messrs. Legge, Holden and Schroeder, in "Thermoplastic Elastomers", published by Hanser Publishers in 1987 (ISBN 3-446-14827-2). Such polymers include thermoplastic polyurethane elastomers and various other block copolymers.

The preferred thermoplastic block copolymers in accordance with the present invention, are styrenic block copolymers, i.e., wherein the or each glassy polymer block of the block copolymer is made of polymerized vinylaromatic monomer, such as styrene, in an amount of at least 80 mole % on the total monomer content of the glassy polymer block. Styrene is the preferred vinyl-aromatic monomer, but other suitable vinylaromatic

monomers include α -methylstyrene, p-methylstyrene,
m-methylstyrene, o-methylstyrene, p-tert-butylstyrene,
dimethylstyrene, and various other alkyl-substituted
styrenes, alkoxy-substituted styrenes, vinylnaphthalene
5 and vinyl xylene. The alkyl and alkoxy groups of the
alkyl-substituted or alkoxy substituted styrenes
respectively preferably contain from 1 to 6 carbon atoms,
more preferably from 1 to 4 carbon atoms. Comonomers, if
present, may be selected from (di)olefins and other
10 compounds copolymerizable with styrene.

Preferred styrenic block copolymers are those wherein
the or each elastomeric polymer block of the block
copolymer is made of polymerized conjugated diene, such
as butadiene or isoprene, in an amount of at least
15 80 mole% on the total monomer content of the elastomeric
polymer block. Butadiene and isoprene are the preferred
dienes, but other suitable conjugated dienes include
dienes with from 4 to 8 carbon atoms per monomer, for
example, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-
butadiene, 1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene,
20 3-ethyl-1,3-pentadiene, and mixtures thereof. Comonomers,
if present, may be selected from vinylaromatic monomers
and other compounds copolymerizable with the diene.

The vinyl content of the elastomeric polymer block
25 (i.e. that part of the conjugated diene that is
polymerized in a "1,2-fashion") is preferably at least
55% (mol/mol on total conjugated diene), more preferably
in the range of 65-80%. These styrenic block copolymers
have greater ease of processing, require even less
30 plasticizer, and add increased melt strength and
drawability to the thermoplastic elastomer composition.

Still more preferred, are styrenic block copolymers
that have at least one elastomeric polymer block made of
polymerized conjugated diene that is hydrogenated. In

other words, the hydrogenated version of the block copolymers mentioned above. Suitably, such block copolymers are selectively hydrogenated (i.e., only the elastomeric polymer blocks), to a degree of 80% or more based on the (original) residual unsaturation.

Excellent synthetic bottle stoppers have been made from styrenic block copolymers having an overall content of vinylaromatic monomer in the range of 10 to 50% by weight, preferably 20 to 45% by weight. Most preferred are such styrenic block copolymers having a total apparent molecular weight in the range from 30,000 to 400,000 g/mol, more preferably from 50,000 to 300,000 as measured with gel permeation chromatography (GPC) using polystyrene calibration standards (according to ASTM D 3536).

Block copolymers come in the form of linear diblocks, triblocks and multiblocks (produced with sequential polymerization techniques or difunctional coupling agents), or branched block copolymers (using multi-functional coupling agents and/or re-initiation techniques). The preferred block copolymers in accordance with the present invention are linear triblock copolymers, or blends of triblock copolymers, containing up to 30% weight/weight of diblock copolymers.

Suitable block copolymers include, amongst others, those sold by Shell under the trademark "KRATON", and those sold under the trademarks "DYNAFLEX" (CC&P), "VECTOR" (DECXO), "EUROPRENE" (ENICHEM); "QUINTAC" (NIPPON ZEON); "FINAPRENE" (FINA); "STEREON" (FIRESTONE); "TUFRENE" (ASAHI) and "SEPTON" (KURARAY). Particularly suitable are "KRATON" elastomeric block copolymers sold as grade D1102, KX225, G1650, G1652, G1657, G1701, G1726, G1730, G1750 and G1780.

Component b)

A branched polyolefin is a polymer having alkyl groups containing 2 or more carbon atoms attached to the backbone. Such polyolefins are known as high melt strength polymers and hence impart high melt strength and drawability to blends thereof with (styrenic) block copolymers. Such branched polyolefins include e.g., high melt strength propylene polymers, containing long-chain branches inside the polypropylene, disclosed by Dr. Ulf Panzer at the SPO '98; and poly-1-butylene as disclosed in e.g., US Patent No. 4,960,820 which is herein incorporated by reference. Suitable polyolefins have a melt flow index ('MFI') of from 0.05 to 400, preferably from 0.1 to 200, even more preferably from 0.2 to 20 and most preferably from 0.4 to 5 dg/min at 2.16 kg/190 °C. They may be produced by the polymerisation of an alpha- or internal alkene having 3 or more carbon atoms using the Daploy process disclosed by Dr. Pzanzer, or by (Ziegler-Natta low pressure) polymerization of an alpha- or internal alkene having 4 to 10 carbon atoms, preferably a linear alkene such as 1-butene, 1-pentene, 2-pentene, 1-hexene, 1-heptene, 1-octene, or the copolymerization of these alkenes with e.g., up to 10 mole% ethene and/or propene (e.g., as described in DE-A-1,570,353). Preferably the branched polyolefin contains from 80%, more preferably from 95% and most preferably from 97% by weight of isotactic portions. Branched polyolefins that have been found to be very suitable are polymers of 1-butene, having a 1-butene content of at least 50 mole%, preferably at least 70 mole%. The most preferred branched polyolefin is poly-1-butene.

The weight average molecular weight of the polyolefin may range from 60,000 to 1,000,000 g/mol, determined by GPC, using poly-1-butene standards. Suitable polyolefins

have a density of from 0.875 to 0.925, preferably from 0.900 to 0.920 and most preferably from 0.910 to 0.915.

5 Poly-1-butene PB-0110, marketed by Shell is a particularly suitable polymer. This polymer is a homopolymer with a melt index of 0.4 g/10min. at 190 °C and 2.16 kg and a weight average molecular weight of 800,000.

10 Component b) is preferably used in an amount of 10 to 100 parts per 100 parts of component a) ('phr'), more preferably in an amount of 30 to 80 phr.

Component c)

15 Plasticisers are well known to those skilled in the art. Typically, the hardness of polymer compound is decreased by adding a plasticiser. The plasticiser is typically substantially compatible with at least the elastomeric polymer blocks of the thermoplastic block copolymer used as component a).

20 Examples of plasticisers commonly used in respect of the preferred elastomeric block copolymers include hydrocarbon oil, preferably naphthenic or paraffinic oil, more preferably paraffinic oil. Examples of alternative plasticisers which may be used in the compound of the invention are, oligomers of randomly or sequentially polymerised styrene and conjugated diene, oligomers of conjugated diene, such as butadiene or isoprene, liquid polybutene-1, and ethylene-propylene-diene rubber, all having a weight average molecular weight in the range from 300 to 35,000, preferably from 300 to 25,000, more preferably from 500 to 10,000.

25 Whereas the presence of such plasticisers in the prior art formulations is essential, as in mentioned herein before with respect to the Supreme Corq bottle stoppers, the presence thereof in the present formulation is only optional, and in the preferred embodiment even absent. If present, then such plasticisers may be used in

an amount of up to 50 phr, preferably in an amount of up to 30 phr, more preferably in an amount of up to 20 phr.

Blowing agent

As noted above the foamed thermoplastic elastomer composition of the present invention also contains a blowing agent. Normally a blowing agent decomposes above a certain temperature thereby releasing gas, such as nitrogen, which causes a volume increase of the reaction mass. The temperature at which the blowing agent starts decomposing is further referred to as the activation temperature. In principle, any known blowing agent such as the ones mentioned above, and more particular as described in US patent No. 5,585,411 may be used. Generally known blowing agents are for instance sodium bicarbonate, azodicarbonamide-based compound and diphenyloxide-4,4'-disulphohydrazide. The latter is commercially available under the tradename "GENITRON" OB, while an azodicarbonamide-based masterbatch is commercially available under the tradenames "GENITRON" PB10 or "CELOGEN" 754A.

Alternative blowing agents are heat expandable thermoplastic particles encapsulating heat expandable gas or liquified gas. Such heat expandable thermoplastic particles are known in the art and available commercially under the tradename "EXPANCEL". Further details regarding such heat-expandable thermoplastic particles can e.g. be obtained from European patent application No. 717,091, which is incorporated herein by reference.

Preferably, the blowing agent is azodicarbonamide or sodium bicarbonate or mixtures thereof. Especially good results may be obtained with sodium bicarbonate.

The blowing agent is preferably present in an amount from 1 to 10 %wt., basis the total composition, more preferably 1 to 5% by weight.

Other components

5 Optionally, the foamed thermoplastic elastomer composition comprises further components. Such other components include the "olefinic rubbers" mentioned in US patent No. 5,585,411; the compatible and incompatible materials mentioned in WO 94/28066, etc.

10 For instance, the composition may further comprise from 5 to 50 phr of a polyolefin other than the branched polyolefin, e.g., selected from polyethylene, polypropylene and copolymers thereof. Preferably, the polyolefin is polypropylene or polyethylene, in particular LLDPE. More preferably, the polyolefin is polypropylene.

15 The foamed thermoplastic elastomer composition may also comprise polymers that are compatible with the glassy polymer blocks of the thermoplastic block copolymers, such as polyphenylene ether and/or polystyrene. For instance, the composition may comprise from 5 to 50 phr of such polymers.

20 It will be appreciated that the compounds of the present invention may further contain additional compounds like stabilisers, fillers, slipping agents (compounds that are known to provide grip to the glass, such as stearates, eureamide and/or kenamide), waxes and colouring agents (pigments) and even bits of natural cork to give the stopper a cork-like appearance.

25 The compositions of the invention can be prepared according to procedures well known to those skilled in the art. For instance they may be made by extrusion and melt blending. Examples of apparatus which may be used to prepare the compositions of the present invention include, but are not limited to, single or multiple screw extruders, mixing rollers, internal mixers; Banbury mills, and kneaders. For example, the compositions of the 30 present invention may be prepared by feeding ingredients

either partly or fully as a pre-blend or separately in a discontinuous or continuous mixer. The mixer is preferably a continuous mixer. If in first instance compositions are produced that do not contain a blowing agent then we prefer a twin-screw extruder is used, in particular a co-rotating twin-screw extruder.

The composition ingredients are preferably pre-blended as follows. If a plasticiser is used, then first the block copolymer is blended with part or all of the plasticiser. The latter is preferred. The plasticiser and block copolymer may be blended by contacting the plasticiser and oil and rolling, tumbling or mixing in suitable apparatus. Alternatively, the block copolymer and plasticiser may be melt mixed using apparatus such as single or multiple screw extruders, mixing rollers, internal mixers, Banbury mills, and kneaders. If pre-blending block copolymer and plasticiser is conducted in an extruder, then the plasticiser is typically metered into the extruder such that the metering rate is matched to the proportion of oil and polymer desired in the final composition.

The pre-blending step is typically carried out in a so-called turbo-mixer, such as a "Papenmeier" mixer.

The block copolymer or blend of block copolymer and plasticiser is then blended with the branched polyolefin (e.g., poly-1-butene), and any other ingredients such as filler, polyolefin, polyphenylene ether, syndiotactic polystyrene, stabilisers, waxes and/or pigments.

Subsequently, blowing agent may be added, either in the same or a separate blending step. Alternatively, and most preferably, no blowing agent is added at this stage and first a composition without blowing agent is produced.

If a composition without blowing agent is produced, then the composition may subsequently be pre-blended or tumble-mixed with a blowing agent to prepare a

masterbatch as will be discussed in more detail herein after.

If a composition with blowing agent is produced, care should be taken that during the compounding process the 5 temperature is kept below the blowing agent decomposition temperature unless (full or partial) foaming is desired during this first step.

The preparation of a foamed thermoplastic elastomer composition as described above comprises a second aspect 10 of the present invention. In order to produce the "cork", the composition is injected into a mould, e.g. as described in US patents Nos. 3,984,022 and/or 4,499,141. Alternatively, the present composition allows corks to be made via extrusion, which is much preferred over 15 injection moulding since producing uniform corks in a continuous fashion at a higher rate. A third aspect of the present invention concerns foamed articles (including, but not limited to corks) obtainable by this preparation.

20 The invention is illustrated by the following examples.

Examples

The following ingredients were used in the Examples:

PF814	a high melt strength polypropylene (MFI = 3, 230 °C/2.16 kg) commercially available from Montell polyolefins.
PB0110	a high melt strength poly-1-butene (MFI = 0.4, 190 °C/2.16 kg; MP is about 125 °C) commercially available from Montell polyolefins.
"PRIMOL" 352	Paraffinic oil.
"KRATON" G1652 ('KG1652')	a linear styrene-ethylene/butylene-styrene block copolymer having a polystyrene content of 29% by weight, available from Shell Chemicals companies.
"KRATON" G1701 ('KG1701')	a linear styrene-ethylene/propylene block copolymer having a polystyrene content of 28% by weight, available from Shell Chemicals companies.
"IRGANOX" 1010	tetrakis-ethylene-(3,5-di-tertiary-butyl-4-hydroxy-hydrocinnamate)methane.
"IRGANOX" PS800	dilauryl thiopropionate.
"GENITRON" PB10	a masterbatch of 10% weight azodicarbonamide in a LDPE carrier, available from Bayer.
"CELOGEN" 754-A	activated azodicarbonamide in powder form, available from Uniroyal Chemicals.

TPE Compositions

Compositions not containing blowing agent were prepared as follows. 100 parts by weight of a KG1652 were blended with a desired amount (0 or 30 parts by weight,

phr) of "PRIMOL" 352 in a Papenmeier mixer for 10 minutes at room temperature.

5 To the pre-blend thus obtained were added the desired amount (0 or 25 phr) of KG1701, a desired amount (27 or 54 phr) of poly-1-butene and a desired amount (0 to 54 phr) of polypropylene and stabilisers. Blending was continued for 5 minutes.

10 The pre-blend thus obtained was fed into a co-rotating twin-screw extruder (Werner-Pfeifferer) to produce various compositions. The temperature in the twin-screw extruder ranged from 140 to 200 °C. The twin-screw extruder is equipped with a strand die. The strands obtained are cooled down in a water bath and cut into pellets with a pelletiser. Table 1 depicts the breakdown 15 of compositions A-D, all in parts by weight.

Table 1

Compound	A	B	C	D
KG1652	100	100	100	100
KG1701		25	25	25
"PRIMOL" 352				30
PB0110	54	54	54	27
PF814		54	27	27
"IRGANOX" 1010	0.2	0.2	0.2	0.2
"IRGANOX" PS800	0.2	0.2	0.2	0.2

Pellets of compositions A and B obtained above were dry-blended with 3% by weight of azodicarbonamide as blowing agent to prepare masterbatches A and B. The blowing agent used in example 1 was "GENITRON" PB10.

20 The masterbatches A and B thus obtained were fed into a single screw lab extruder (Extrudex), using a temperature profile of 190 °C at the feed entrance, 200 °C at the end of the extruder and 210 °C at the die, to prepare foamed compositions A and B. The die was a

strand die of 6 mm. The density of the foamed strands obtained and the compounds prior foaming were measured. Results are shown in Table 2.

Table 2

Compound	Density
A prior foaming	0.90
A + 3% blowing agent	0.66
B prior foaming	0.91
B + 3% blowing agent	0.54

Both compositions A and B show a good density decrease with 3% of blowing agent. The best density decrease is obtained with composition B containing a mixture of triblock and diblock copolymers.

Example 2

Pellets of compositions A and B obtained in example 1 were dry-blend with 2.5 or 3% by weight of "GENITRON" PB10 as a blowing agent to prepare masterbatches.

The masterbatches thus obtained were fed into an injection moulding machine (Battenfeld), using a temperature profile of 190 °C at the feed entrance 200 °C at the end of the extruder and 210 °C at the die, to prepare foamed specimen A and B. The foamed specimen obtained by the injection were circular plates with a diameter of 45 mm and a thickness of 6 mm. The density of the foamed specimen were measured and the results are shown in Table 3.

Table 3

Composition	Density
A + 2.5% blowing agent	0.53
B + 2.5% blowing agent	0.52
B + 3% blowing agent	0.52

Both compounds show good density decrease with 2.5% by weight of blowing agent and an increase of blowing agent did not result in a decrease of the density.

Example 3

5 Pellets of compositions A, C and D were dry-blended with 5% by weight of azodicarbonamide as blowing agent to prepare masterbatches A, C and D. The masterbatch A and C has been prepared with the blowing agent "GENITRON" PB10. The masterbatch D has been prepared with the blowing agent "CELOGEN" 754-A.

10 The masterbatches A, C and D thus obtained were fed into an injection moulding machine (Negri Bossi & C), using a temperature profile of 170 °C at the feeding entrance, 190 °C at the end of the extruder and 190 °C at 15 the die to prepare foamed specimens A and C. The temperature profile was 160 °C at the feeding entrance and 180 °C at the end of the extruder and at the die to prepare specimens D. The foamed specimens obtained were stoppers of 38 mm by length and a diameter of 22 mm. The 20 density of the stoppers were measured and the results are shown in Table 4.

Table 4

Composition	Density
A + 5% blowing agent	0.63
C + 5% blowing agent	0.56
D + 5% blowing agent	0.54

The best density decreases were obtained with compositions C and D, containing linear styrene-ethylene/propylene block copolymer.

25 The foaming conditions have not been optimised in examples 2 and 3. For instance, optimisation of foaming conditions such as optimum temperature profile and die

pressure is expected to lead to further density reduction to e.g. 0.5.

It is known that poly-1-butene crystallises only slowly. If desired, nucleating agents may be used to 5 increase the crystallisation rate. Nucleating agents are well known to those skilled in the art and available commercially. The most popular nucleating agent is Talc, but the use of stearamide is also well known.

Example 4

10 Foamed stoppers C and D thus obtained in example 3 have been inserted in glass bottles filled with water, using a manual cork insertion machine. An ordinary corkscrew was then fixed into the stoppers. The bottles have been then fixed in a tensile machine (Zwick) while 15 the corkscrew was fixed at the moving crosshead. The stoppers were pull-out of the bottle at a constant speed of 100 mm/min. The force needed to extract the stoppers was measured and the wall-stress was calculated with the stopper length and the bottle circumference. The stoppers 20 C and D have been measured in comparison with natural cork of 3 and 5 years old and in comparison with competitor synthetic stoppers X and Y, having both a density of 0.60. The results are shown in Table 5.

Table 5

Stoppers	Force N	Wall Stress, kPa
Natural cork 3 years	247	156
Natural cork 5 years	395	153
Competitor X	230	110
Competitor Y	180	70
Stopper C	410	184
Stopper D	230	112

The curves obtained during the tensile test are shown in figure 1. The results and the graph show that stopper C is closer to the natural cork of 3 or 5 years.

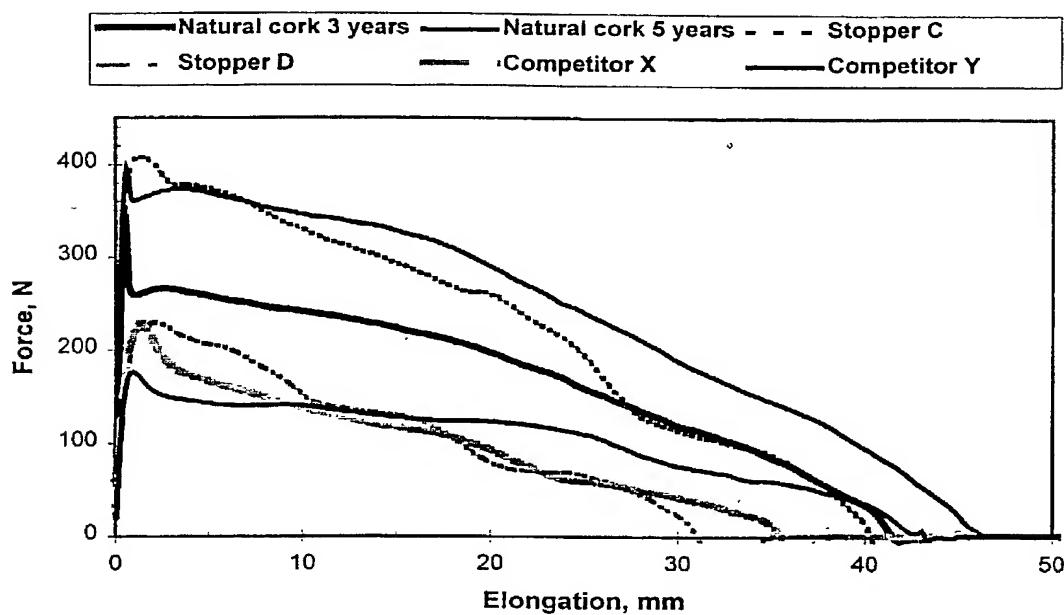


Figure 1

C L A I M S

1. A synthetic bottle stopper made from a foamed thermoplastic elastomer composition comprising
 - a) one or more thermoplastic block copolymers
 - c) a blowing agent, and optionally
 - d) one or more plasticisers,characterised in that the composition further comprises
 - b) one or more branched polyolefins having a melt flow index of from 0.05 to 400 (at 2.16 kg/190 °C, determined in accordance with ASTM D 1238).
- 10 2. A synthetic bottle stopper as claimed in claim 1, comprising one or more styrenic block copolymers as component a), wherein the or each styrenic block copolymer contains one or more glassy polymer blocks made of polymerized vinylaromatic monomer in an amount of at least 80 mole% on the total monomer content of the block and having one or more elastomeric polymer blocks made of polymerized conjugated diene in an amount of at least 80 mole% on the total monomer content of the block.
- 15 3. A synthetic bottle stopper as claimed in claim 2, wherein the vinylaromatic monomer is styrene and wherein the diene is butadiene and/or isoprene.
- 20 4. A synthetic bottle stopper as claimed in claims 2 to 3, wherein the or each styrenic block copolymer has an overall content of vinylaromatic monomer in the range of 10 to 50% by weight, and a total apparent molecular weight in the range of from 30,000 to 400,000 g/mol.
- 25 5. A synthetic bottle stopper as claimed in claims 1 to 4, wherein component a) comprises a triblock polymer or a mixture of a diblock and triblock copolymer.

6. A synthetic bottle stopper as claimed in claims 1 to 5, wherein component b) comprises a polymer of 1-butene and/or a high melt strength polymer of propene.

5 7. A synthetic bottle stopper as claimed in claim 6, comprising component b) in an amount of 10 to 100 parts by weight per 100 parts by weight of component a).

8. A synthetic bottle stopper as claimed in claims 1 to 7, comprising a blowing agent in an amount from 1 to 10 %wt, basis the total composition.

10 9. A process for preparing a foamed thermoplastic elastomer composition comprising

- a) one or more thermoplastic block copolymers
- b) one or more branched polyolefins having a melt flow index of from 0.05 to 400 (at 2.16 kg/190 °C, determined

15 in accordance with ASTM D 1238)

- c) a blowing agent, and optionally
- d) one or more plasticisers,

wherein components a) to d) are fed either partly or fully as a pre-blend or separately in a discontinuous or

20 continuous mixer.

10. A foamed article obtainable by the process of claim 9.

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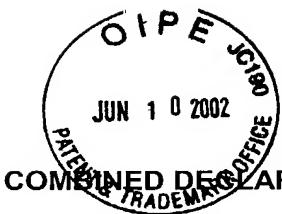
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(54) Title: SYNTHETIC BOTTLE STOPPER

(57) Abstract: The present invention provides a synthetic bottle stopper made from a foamed thermoplastic elastomer composition comprising: a) one or more thermoplastic block copolymers c) a blowing agent, and optionally d) one or more plasticisers, characterised in that the composition further comprises b) one or more branched polyolefins having a melt flow index of from 0.05 to 400 (at 2.16 kg/190 °C, determined in accordance with ASTM D 1238).



Atty. Dkt. No. KPTS/6648

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

This declaration is of the following type:

- original
- divisional
- continuation
- continuation-in-part

INVENTORSHIP IDENTIFICATION

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SYNTHETIC BOTTLE STOPPER

SPECIFICATION IDENTIFICATION

The specification of which:

- is filed herewith
- was filed on _____, under Serial No. _____, executed on even date herewith; or
- Express Mail No.(as Serial No. not yet known) and was amended on _____ (if applicable)
- was filed in PCT International Application No. PCT/EP00/06354 on July 4, 2000, and is identified as U.S. Serial No. 10/030,438.

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information I know to be material to patentability in accordance with Title 37, Code of Federal Regulations, §1.56, and which is material to the examination of this application; namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent.

- In compliance with this duty there is attached an Information Disclosure Statement in accordance with 37 CFR §1.98.

PRIORITY CLAIM (35 U.S.C. §119)

I hereby claim foreign priority benefits under Title 35, United States Code, §119, of any provisional or foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below, and have also identified below any provisional or foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

No such applications have been filed.
 Such applications have been filed as follows:

A. Prior foreign/PCT application(s) filed within 12 mos. (6 mos. for design) prior to this application, and any priority claims under 35 USC §119

<u>Country/PCT</u>	<u>Application Number</u>	<u>Date Filed</u>	<u>Priority Claimed</u>
EP	99305309.9	5-Jul-99	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No <input type="checkbox"/> Yes <input type="checkbox"/> No <input type="checkbox"/> Yes <input type="checkbox"/> No

B. All foreign application(s), if any, filed more than 12 mos. (6 mos. for design) prior to this U.S. application

<u>Country/PCT</u>	<u>Application Number</u>	<u>Filing Date</u>
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C. U.S. Provisional Application filed within 12 months prior to this application

<u>Serial Number</u>	<u>Filing Date</u>
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PRIORITY CLAIM (35 USC §120)

I hereby claim the benefit under Title 35, United States Code, §120, of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information that is material to the examination of this application (namely, information where there is substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application.

No such applications have been filed.

1 2-00
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Inventor's signature: Kadri Date: 19-04-2002
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POWER OF ATTORNEY

I hereby appoint the following attorneys and/or agents to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and, further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Sec. 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patents issued thereon.

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